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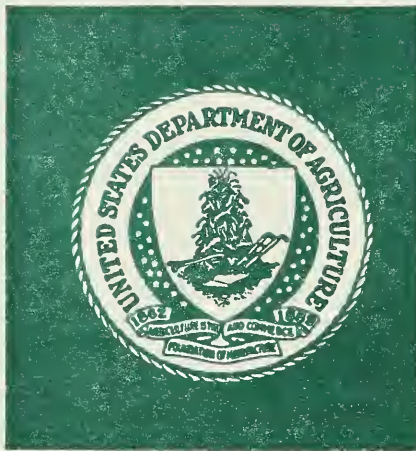
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Introduction

Weathering of outdoor fabrics is a major consideration in their useful lifetime. Previous studies (2,4,8,9,10) have indicated the need for finishes to extend the lifetime of these fabrics. The finishes currently used for this purpose, for example water proofing and rot resistance, are usually effective in preventing certain types of weathering changes from occurring. These finishes also change other properties of the fabrics, such as sunlight resistance, to the point that there is not a great extension of useful lifetime. It is therefore a current and urgent need to develop alternate means of protecting cotton fabric from sunlight degradation. Since the mechanism by which treated and untreated cotton fabrics degrade could be a guide to the development of new finishes, investigation which might provide additional information in this area was deemed desirable.

Considerable research data relating to effects of sunlight on the physical properties of outdoor fabrics has been reported by several researchers (1,10,11,12). It was therefore of interest to better understand the chemical nature of the fabrics, finishes and the various types of weathering. This report deals with photo-degradation of cotton tentage fabric untreated and treated with four different finishes. The four finishes were polyethylene, chlorinated polymer, chlorinated polymer plus antimony oxide, and trimethylol resin. The primary thrust of the investigation dealt with the identification and comparison of pyrolysis products of the exposed and unexposed treated and untreated fabrics. This

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comparison shows the effect of photo-degradation of the fabrics and finishes on their interaction during pyrolysis.

Experimental

An 8.8 oz/yd² cotton duck fabric was selected for the project. Four different finishes were applied to the fabric at the Cotton textile Chemistry Laboratory - Southern Regional Research Center under the supervision of Dr. Robert Harper. These finishes and add-ons are 4.8% poly ethylene, 10.1% chlorinated polymer, 12.2% chlorinated polymer plus 12.2% antimony oxide and 11.6% trimethylol resin (Table I).

Xenon Arc Exposure

The experimental fabrics were subjected to 200 hours of Xenon-arc exposure in an Atlas Weather-O-Meter in order to simulate the effect of sunlight exposure. The temperature was maintained at 90° F and the relative humidity at 65%.

Infrared Analysis

The exposed and unexposed fabrics were examined using two different infrared spectrophotometric techniques. First, specimens of the fabric were sandwiched against a KRS-5 crystal and the infrared spectral characteristics of the fabric surfaces were determined using a Wilkes double-beam multiple-internal reflectance (MIR) apparatus mounted in the sample compartment of a Beckman 18A infrared spectrophotometer. Secondly, samples of the finish were eluted from the fabrics directly onto KRS-5 crystals using methanol as the elutant. The methanol was allowed to evaporate leaving the finish as a thin film of residue on the crystal. The infrared spectra of the samples were then obtained using the MIR apparatus.

TABLE 1: DESCRIPTION OF FABRIC AND FABRIC FINISHES

Fabric Number	Add-On	Description
7311-104	--	Untreated control, 8.8 oz/yd ² Desized, scoured, and bleached.
7311-105	4.8%	Polyethylene finish
7311-106	10.1%	Chlorinated polymer finish
7311-107	12.2% 12.2%	Chlorinated polymer finish Antimony oxide finish
7311-108	11.6%	Trimethylol resin finish

Pyrolysis - Gas Chromatography

In order to evaluate any possible change in the pyrolysis products of the fabric by the finishes and/or degradation by light, samples of the fabrics were pyrolyzed into a gas chromatograph and the resultant pyrolysis products separated. The pyrolysis was achieved using a Perkin-Elmer Pyroprobe 100. The sample size was approximately 5 mg of fabric placed inside a quartz tube. The quartz tube was placed in a heater coil probe that was designed to fit into the injection port of a gas chromatograph. The gas chromatograph used was a Perkin-Elmer Model 3920 equipped with a flame ionization detector. The pyroprobe was placed in a preheated injection port and pyrolyzed directly into the injection chamber. The pyrolysis conditions and gas chromatographic separation conditions are given in Table II.

Mass Spectrometry

Mass spectral analysis of the pyrolysis products was accomplished using a DuPont 21-491 B mass spectrometer coupled with a Finnigin Mini-Computer data system. The samples were pyrolyzed into a Varian 2700 gas chromatograph and separation of the components was achieved using the same column previously described in Table II. The effluent from the chromatograph was fed directly into the mass spectrometer. Each chromatographic peak was scanned and the resultant mass spectra were fed into the data system for storage and subsequent analysis.

Results

The exposure of the fabrics to 200 hours xenon arc radiation resulted in obvious physical changes in some of the fabrics. The unfinished fabric (7311-104) remained soft and showed little discoloration. The fabric finished with polyethylene (7311-105) also had no significant changes in



TABLE II: The OPERATING CONDITIONS FOR PYROLYSIS AND GAS CHROMATOGRAPHYPYROPROBE 100

Ramp: 0.1°C/msec
Interval: 20 seconds
Final Temperature: 900°C

3920 GAS CHROMATOGRAPHY

Column: 9' x 1/8" Copper Column Containing 80/100 Mesh Porapak-Q
Helium Flow Rate: 30 psig
Air Flow Rate: 50 psig
Hydrogen Flow Rate: 20 psig
Injection Port Temp.: 220°C
Interface Port Temp.: 220°C
Linear Temp. for Column:
 Initial Temp.: 60°C for 4 Minutes
 Heating Rate : 4°C/Minute
 Final Temp. : 210°C for 80 Minutes
Detector: Flame Ionization Detector (F.I.D.)

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Chart Speed: 5 MM/Minute
Range/Span : 5mv

hand or color. The fabrics finished with chlorinated polymer had a quite drastic change in color. The fabric with the chlorinated polymer (7311-106) changed color on the surface directly exposed to the Xenon-arc from an off-white to light gold. The back side of the fabric showed no color change. The fabric with the chlorinated polymer and antimony oxide (7311-107) finish turned from an off-white to a beige color on both sides of the fabric. The fabric finished with trimethylol resin (7311-108) showed no visible physical changes. Since the object of the research project was to evaluate chemical aspects of the finishes physical changes in the fabrics were not evaluated.

Infrared Analysis

Specimens of each of the exposed and unexposed fabrics were examined by two infrared techniques. The infrared spectra obtained from the removal of surface finish using the M.I.R. - IR techniques indicated no significant differences between the exposed and unexposed fabric finishes for each type of finished fabric. Further analysis of the fabrics using the surface M.I.R. technique again showed no differences in IR spectra between the exposed and unexposed fabrics for each type of finished fabric. Further efforts were not fruitful in determining the effect of the xenon-arc radiation on the character of the finish by infrared techniques due to lack of sensitivity of the equipment available.

Pyrolysis-Gas Chromatography

Previous studies (5,6,7,12) have shown that chemical finishes affect the pyrolysis behavior of cellulose and in particular cotton. It was therefore of interest to compare the pyrolysis behavior of the finished fabrics. Comparison of the pyrolysis products as separated by gas

chromatography can be made between the exposed and unexposed fabrics as well as among the different finished fabrics.

Chromatograms of the pyrolysis products of the fabrics have been reduced in size and are shown in Figures 1-11. Figure 1 shows a chromatogram resulting from the pyrolysis of cotton fabric wherein the peaks are numbered. These chromatograms indicate that the presence of finish does affect the nature of the pyrolysis products for three of the finished fabrics but not for the fabric finished with polyethylene. The pyrolysis-gas chromatogram of the polyethylene finished fabric, Figure 4, is essentially identical to that of the unfinished control fabric, Figure 2, with respect to the components present. However, two components were of a higher relative concentration in the pyrolysis chromatogram of the polyethylene finished fabric vs the untreated control. These two peaks occurred at retention times of 8 minutes and 37 minutes and are marked as peaks 4 and 27 in Figure 1. Peak 4 has been identified as propylene and peak 27 as methylisopropenyl ketone. The rest of the pyrolysis components of these two fabrics were of similar concentration.

Comparison of the chromatograms from the pyrolysis of the fabric finished with chlorinated polymer, Figure 6, with that from the untreated fabric indicate the presence of two new components at retention time of 10, 20 and 106 minutes with a relative reduction in size of the component at 34 minutes retention time (peak 27 on Figure 1) and a large increase in area of the component peak at 49 minutes (peak 39 on Figure 1). The new peak appearing at 106 minutes retention time has a relatively large peak area and appears only in the pyrolysis of the two fabrics containing chlorinated polymer.

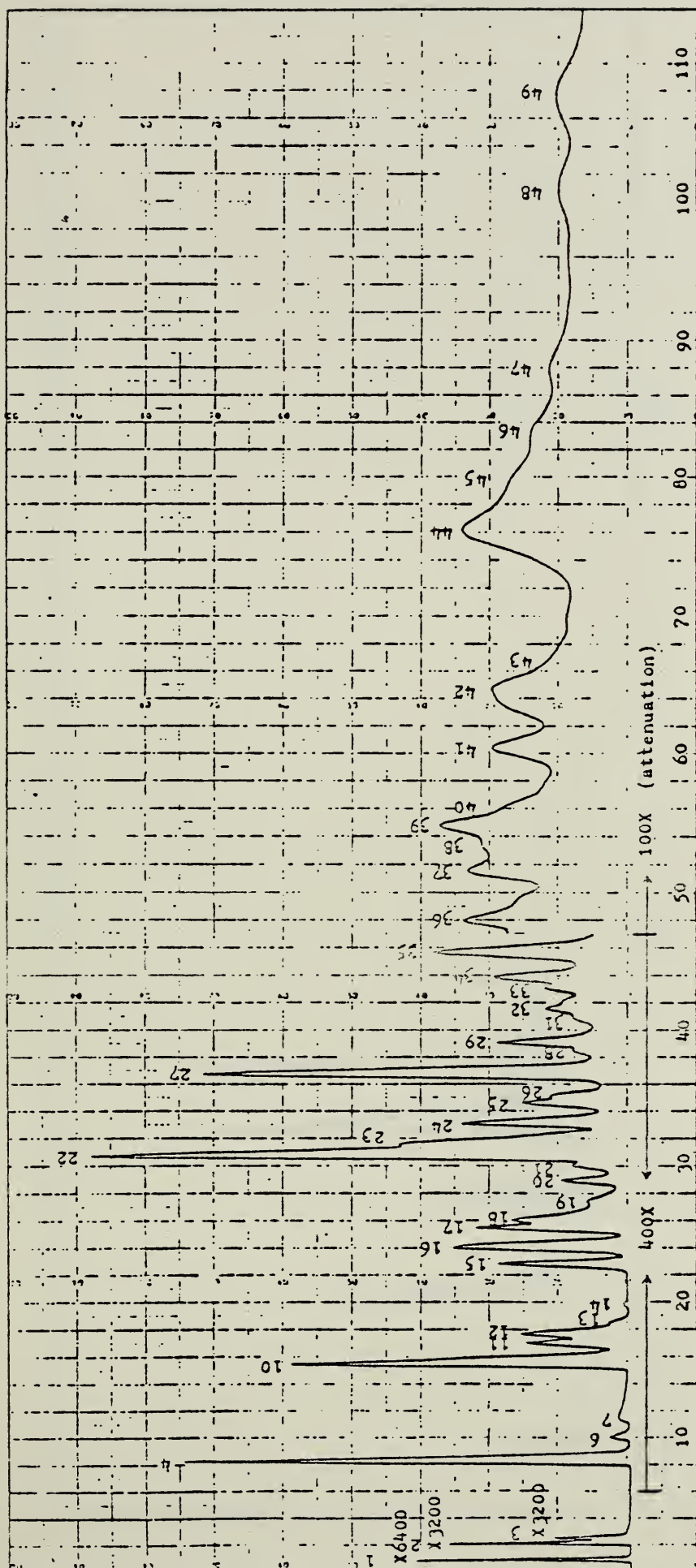


FIGURE 1. Gas chromatogram of pyrolysis products of untreated cotton pyrolyzed at 900°C.

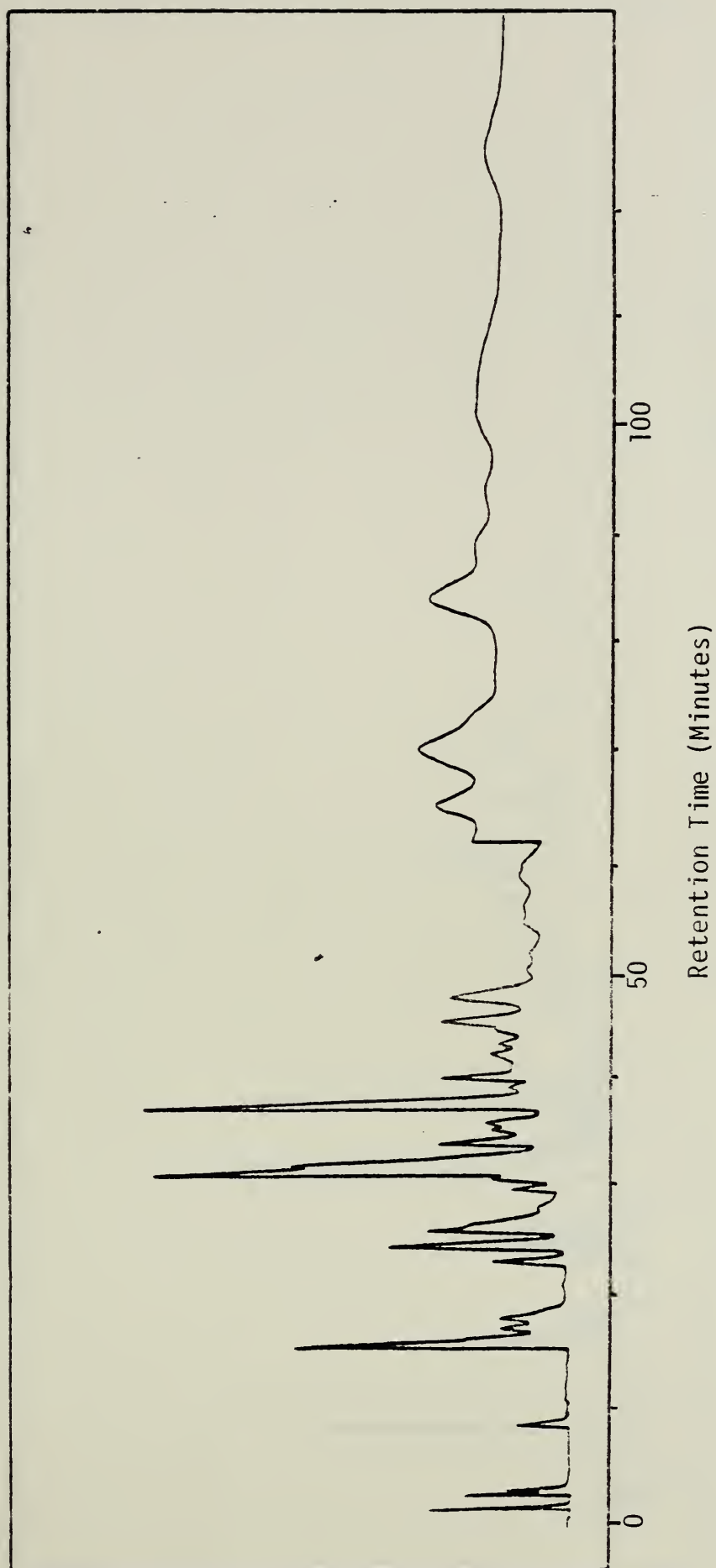


FIGURE 2. Gas chromatogram of pyrolysis products of untreated cotton duck fabric number 104.

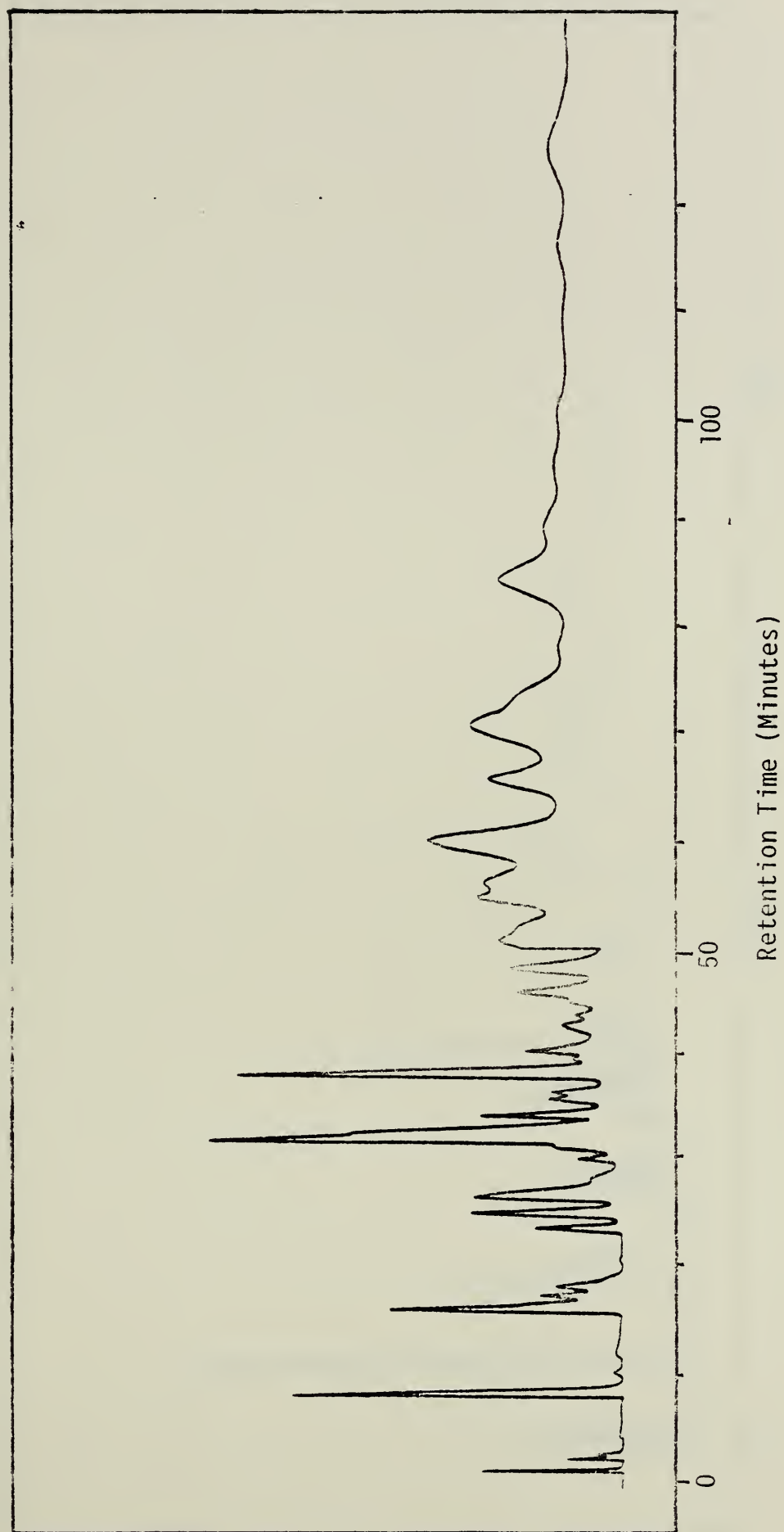


FIGURE 3. Gas chromatogram of pyrolysis products of untreated cotton duck fabric number 104 after 200 hours xenon-arc exposure.

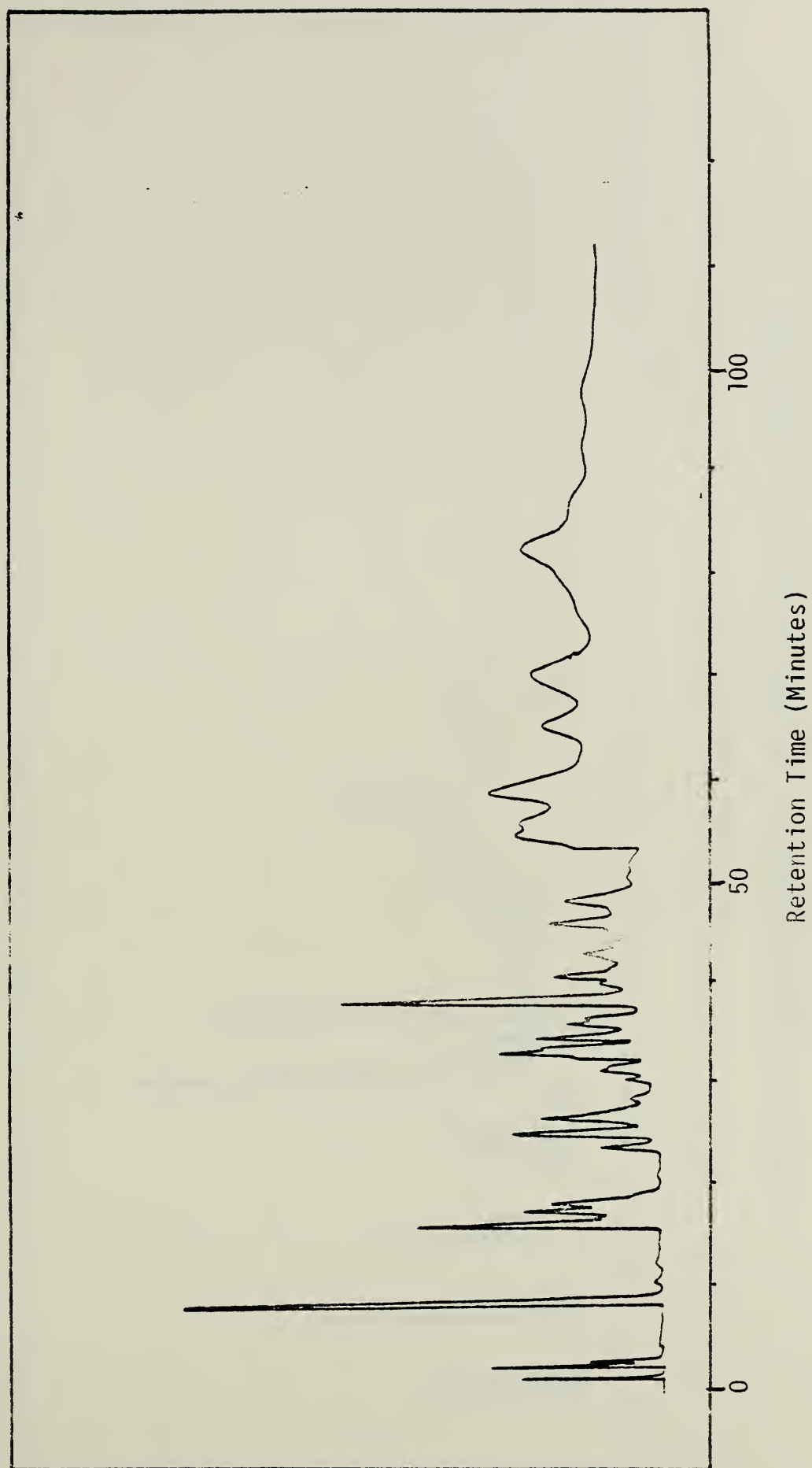


FIGURE 4. Gas chromatogram of pyrolysis products of cotton duck fabric number 105 treated with polyethylene finish.

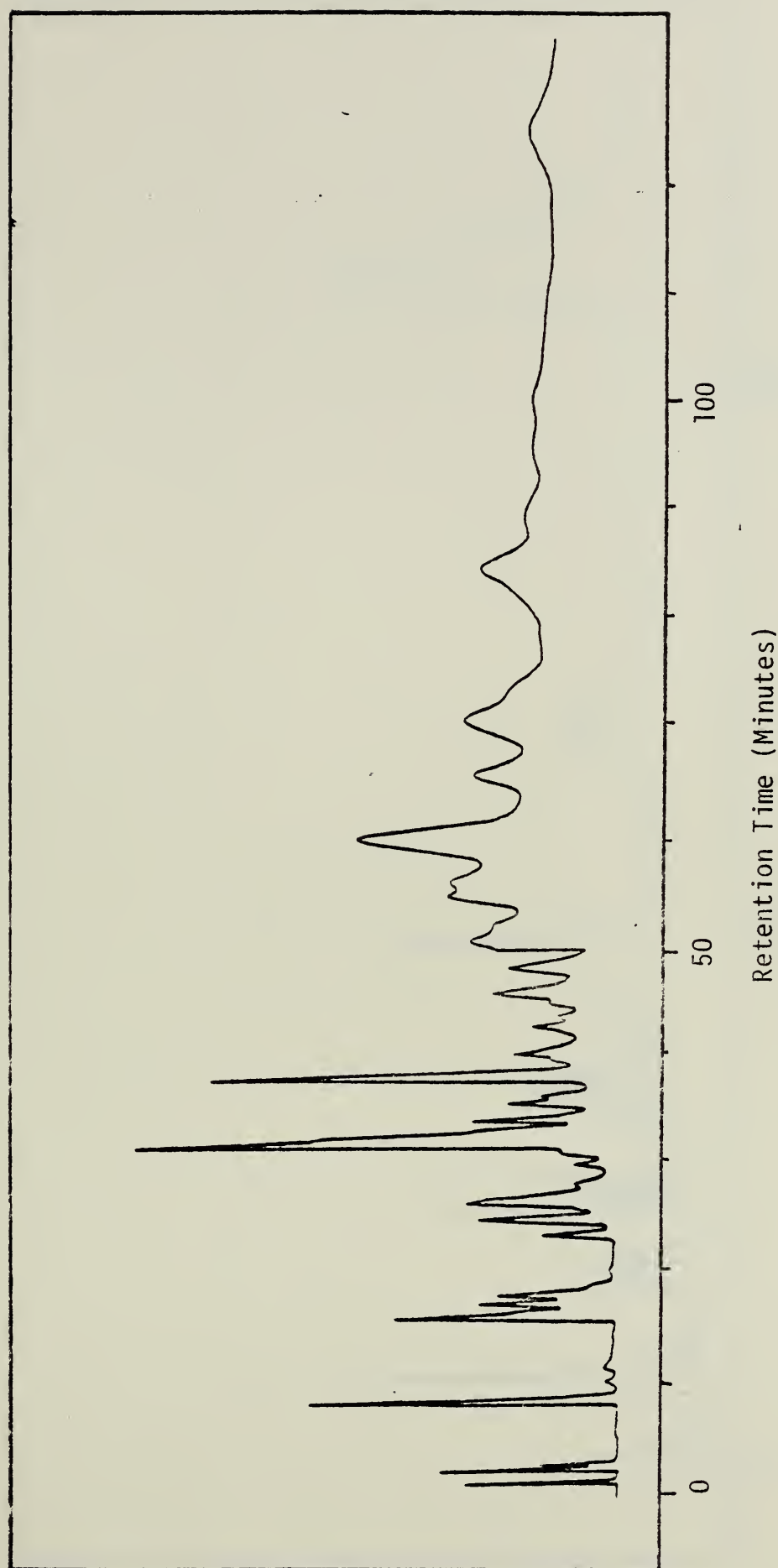


FIGURE 5. Gas chromatogram of pyrolysis products of cotton duck fabric number 105 treated with polyethylene finish after 200 hours xenon-arc exposure.





FIGURE 6. Gas chromatogram of pyrolysis products of cotton duck fabric number 106 treated with chlorinated polymer finish.



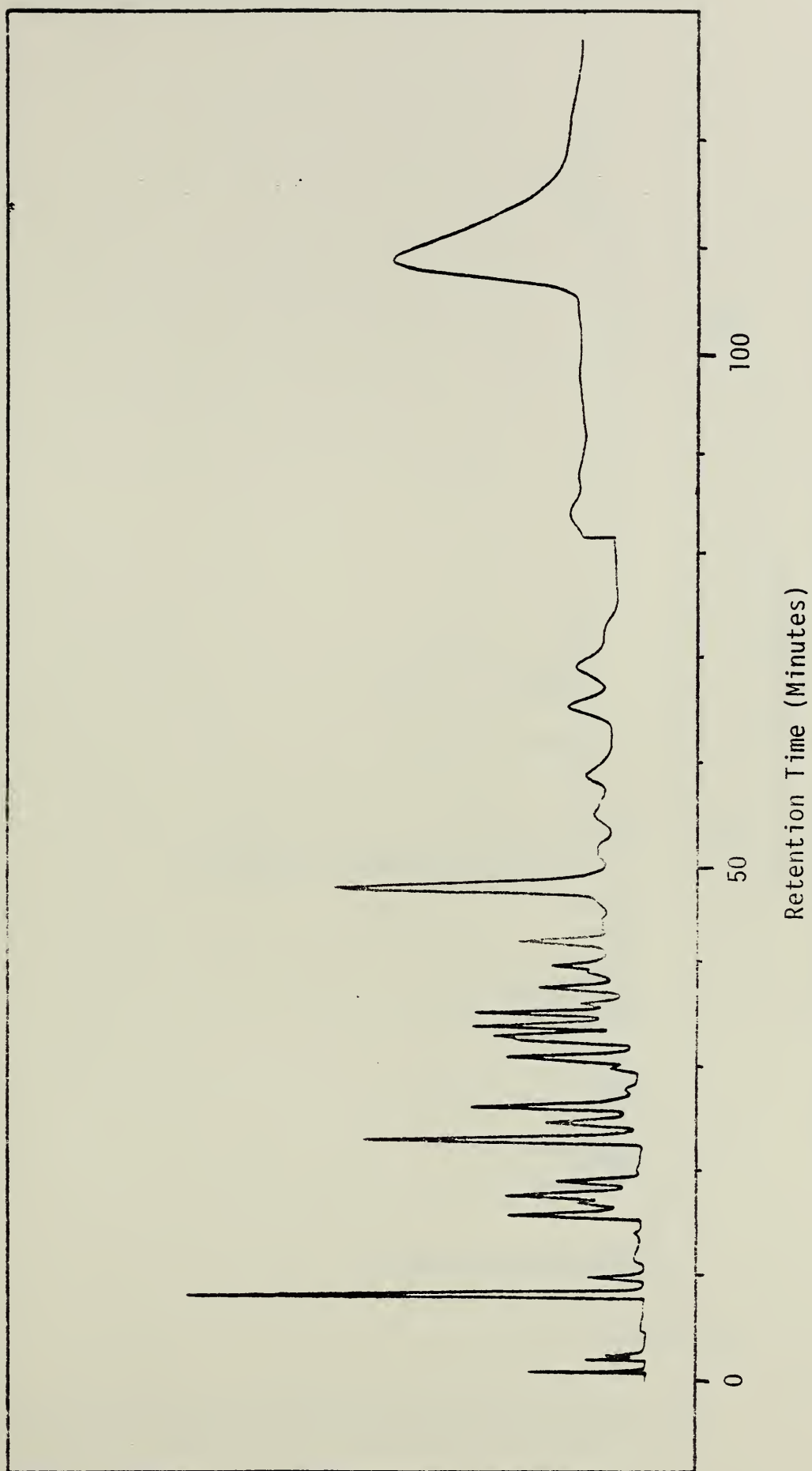


FIGURE 7. Gas chromatogram of pyrolysis products of cotton duck fabric number 106 treated with chlorinated polymer finish after 200 hours xenon-arc exposure.



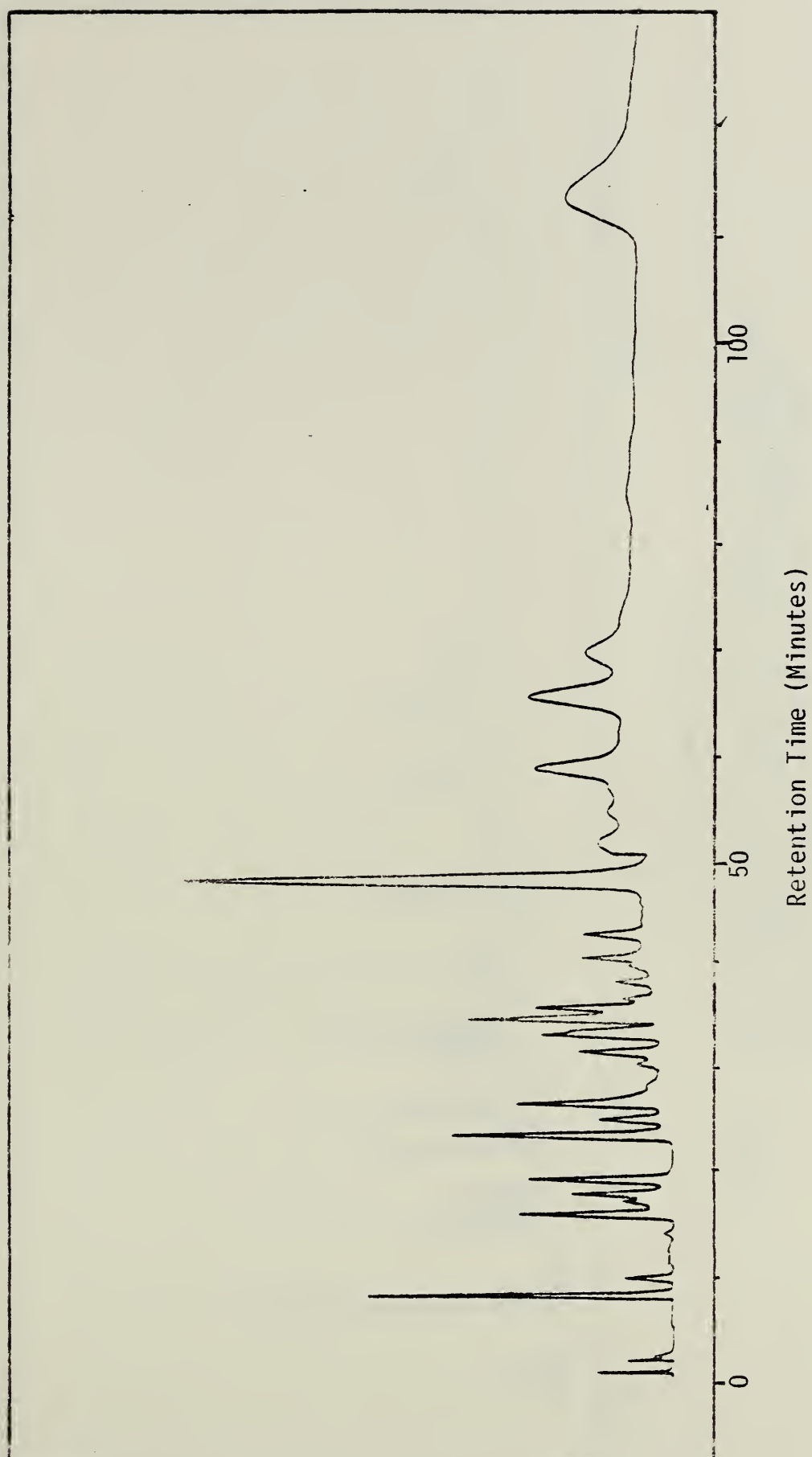


FIGURE 8. Gas chromatogram of pyrolysis products of cotton duck fabric number 107 treated with chlorinated polymer fabric and antimony oxide finish.



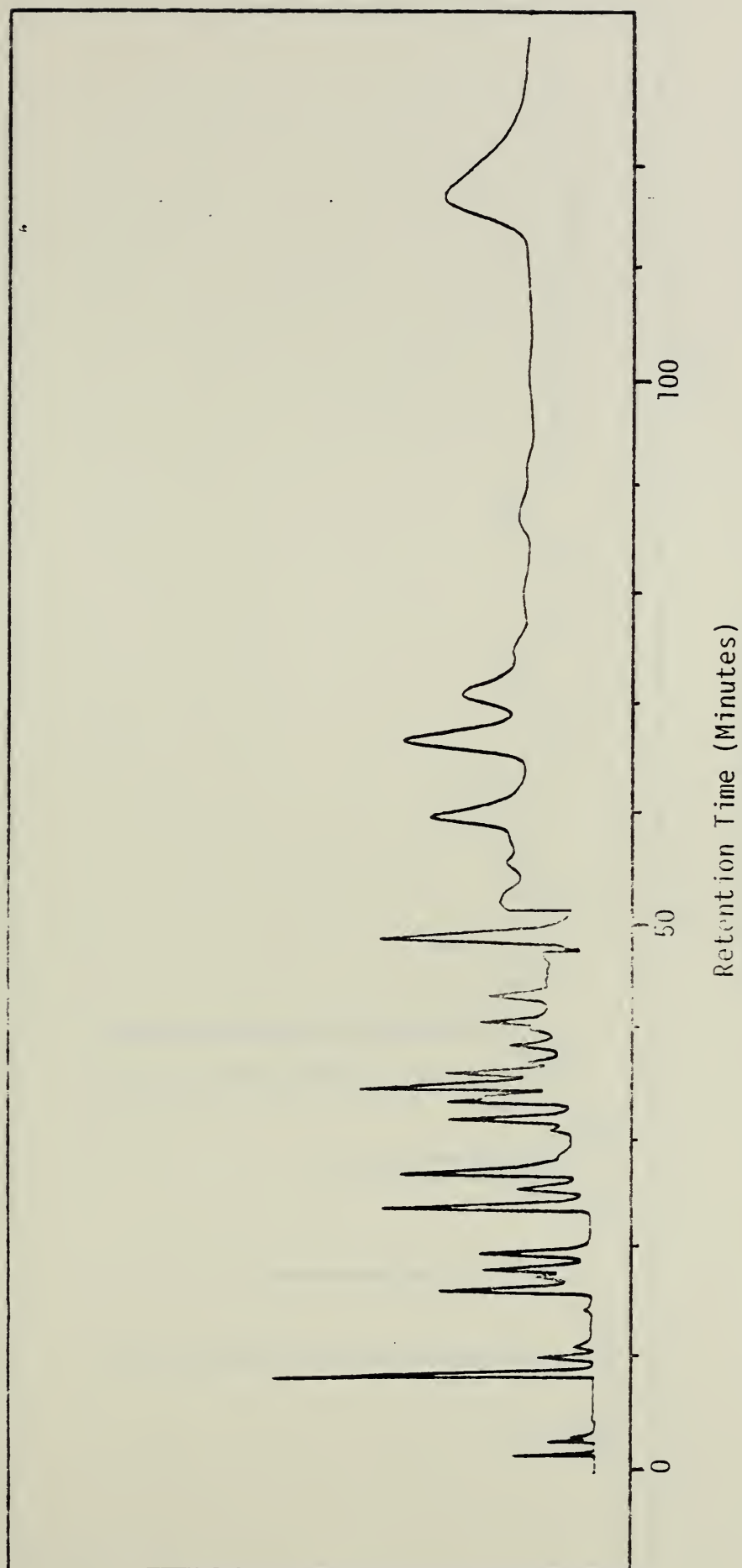


FIGURE 9. Gas chromatogram of pyrolysis products of cotton duck fabric number 107 treated with chlorinated polymer finish and antimony oxide finish after 200 hours xenon-arc exposure.



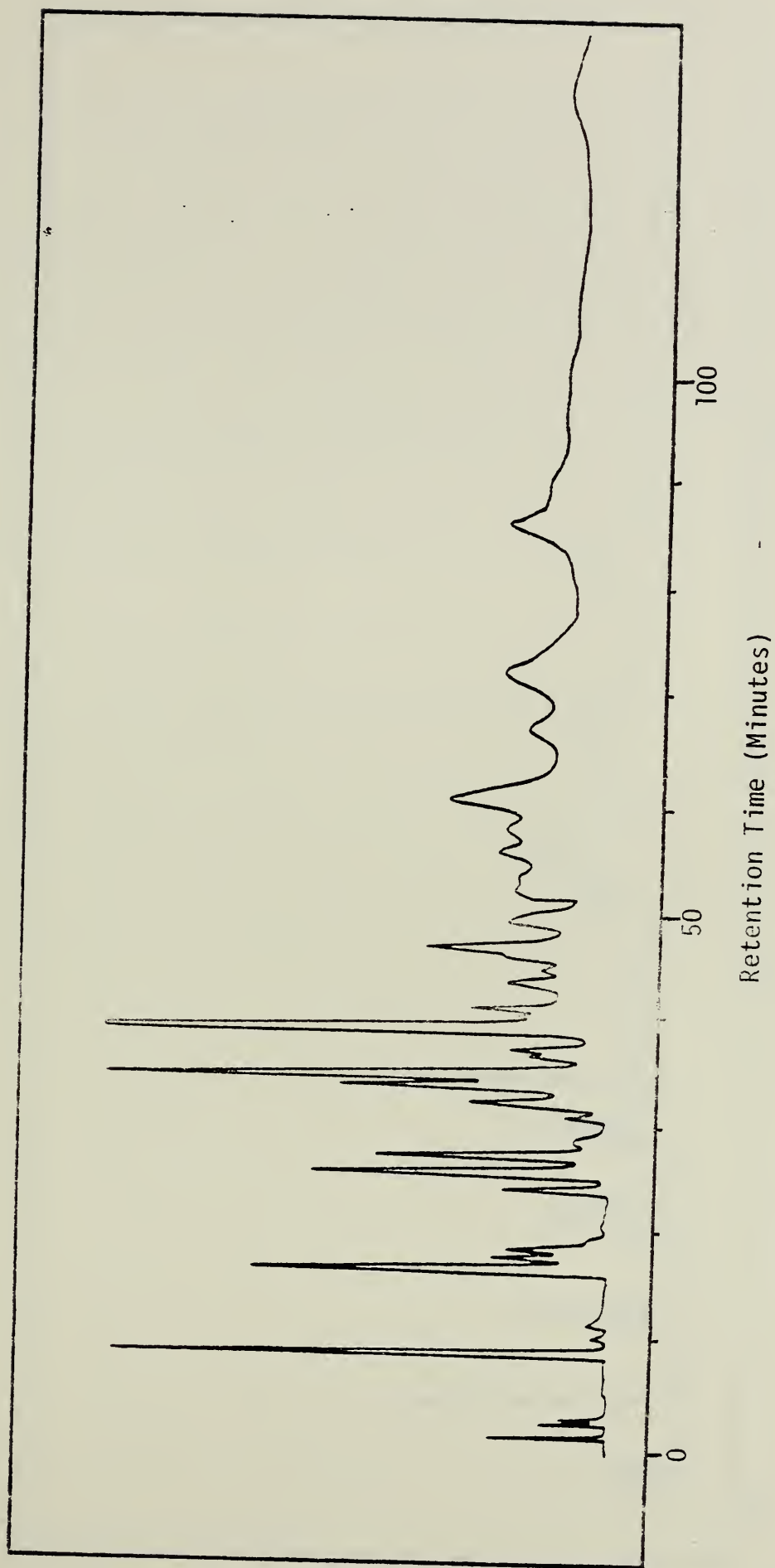


FIGURE 10. Gas chromatogram of pyrolysis products of cotton duck fabric number 108 treated with trimethylol resin finish.



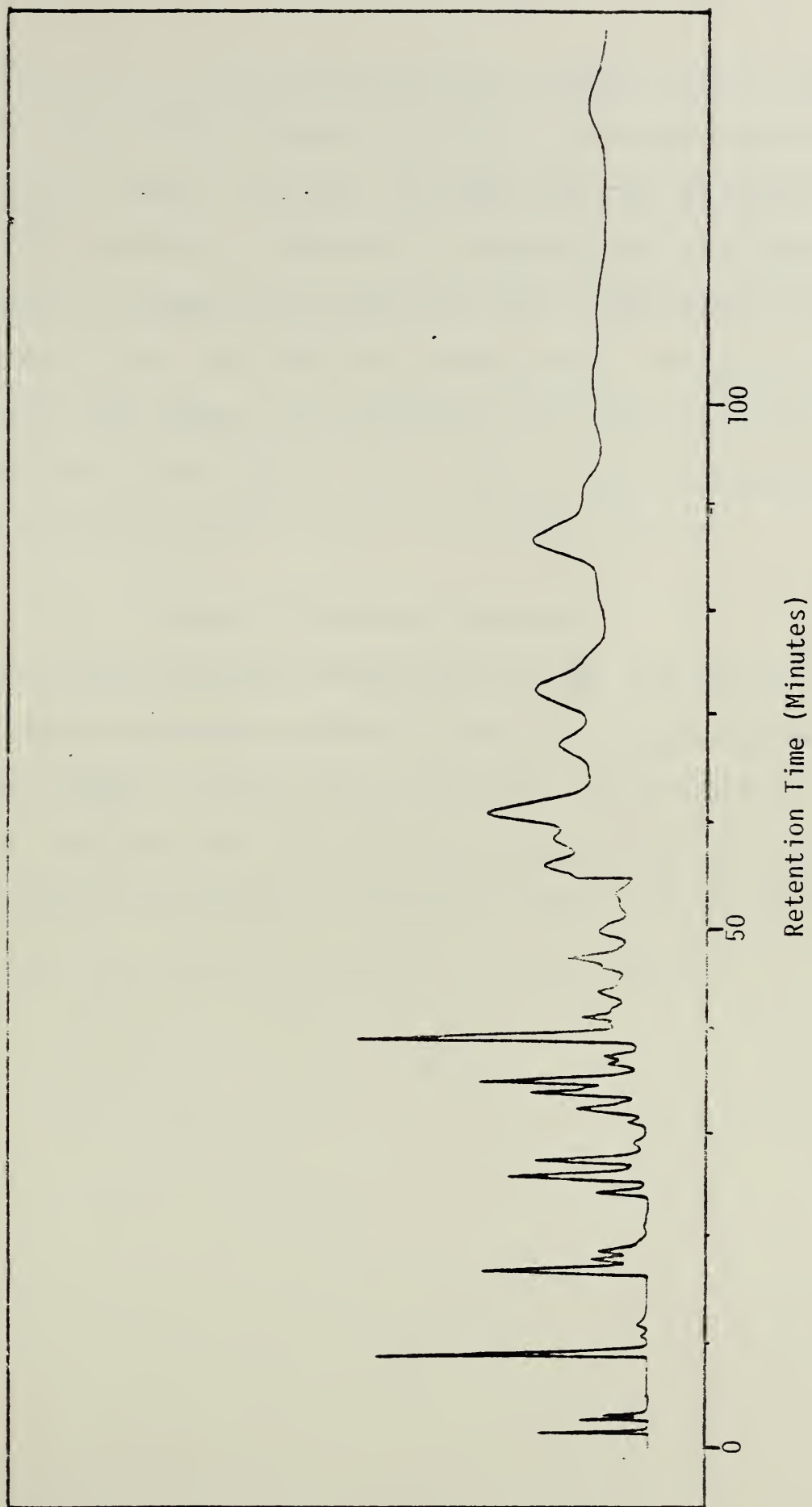


FIGURE 11. Gas chromatogram of pyrolysis products of cotton duck fabric number 108 treated with trimethylol resin finish after 200 hours xenon-arc exposure.



The combination of chlorinated polymer and antimony oxide in the finish on the cotton fabric produced a pyrolysis chromatogram containing peaks identical to those of the fabric finished with only the chlorinated polymer with two exceptions. The peak at a retention time of 49 minutes was significantly increased in size while the peak at 106 minutes was greatly reduced in size. The pyrolysis chromatogram of the fabric finished with trimethylol resin showed a disappearance of the peak at 31 minutes retention time (peak 22 on Figure 1) and a large increase in the size of the peaks at 33 minutes (peak 24) and at 39 minutes (peak 27).

Effect of Xenon-Arc Exposures

Comparison of the pyrolysis-chromatograms for the five fabrics before and after exposure to 200 hours xenon-arc light in a weather-o-meter shows no significant changes in either the pyrolysis products or their relative ratios within a chromatogram. Thus xenon-arc exposure resulted in no appreciable change in the molecular structure of the fabrics or finishes that would alter their pyrolysis behavior in helium atmosphere.



Mass Spectra Analysis

Results of the mass spectra analyses were inconclusive. Table III lists the probable identification of most of the pyrolysis products resulting from untreated cotton fabric. The peak numbers correspond to the respective peaks shown in Figure 1.

As indicated in the previous section there were only a few differences in the type or relative proportion of the pyrolysis products with the addition of the different finishes. There were no new products as a result of the xenon-arc exposure.

The pyrolysis products of cotton (Table III) show a wide range of lower molecular weight compounds. The identification of many of these products required a confirmation of the mass spectral information with the matching of retention times of known compounds. Whenever known compounds did not exist or were not available a greater uncertainty exists about the absolute identity of the compound. This was the case for the new products formed as a result of the presence of finish. All the samples were pyrolyzed and the mass spectra data of the products were stored in a data system over a length of time due to frequent breakdown of the mass spectrometer. This proved to be a major difficulty in analysis of some of the data due to changes in calibration parameters within the instrumentation system. A limited analysis from the data system was achieved for all the fabric analyses but subsequent rechecks and further comparison of the mass spectra with master data files proved impossible.



TABLE III: IDENTIFICATION OF VOLATILE PYROLYSIS PRODUCTS FOR UNTREATED COTTON

GC Peak	Retention Time	Compounds Identified	Molecular Weight
1	0.8	Methane	16
2	2.0	Ethylene	28
3	2.5	Ethane	30
4	8.2	Propylene	42
6	9.7	Allene (Propadiene)	40
7	10.1	Propyne	40
8	12.5	Dimethyl Ether	46
9	14.4	Methyl Alcohol	32
10	15.4	Acetaldehyde	44
11	17.2	Formaldehyde	30
11	17.2	1-Butene	56
12	17.8	1,3-Butadiene	54
12	17.8	Acrolein	56
12	17.8	Glycoaldehyde	60
13	18.8	-----	--
14	19.8	1,2-Butadiene	54
15	----	Ethanol	46
15	23.0	Furan	68
16	24.0	Propionaldehyde	58
16	24.0	----	56
17	25.6	Acetone	58
17	25.6	2-Methyl-2-Butene	70
18	26.2	2-Methyl-1-Buten-3-Yne	66
18	26.2	Methyl Acetate	74
19	27.5	-----	66
20	28.9	Trans,2-Penten-4-Yne	66
20	28.9	Ally Alcohol	58
21	30.3	2-Methyl Propenal	70
22	31.0	2-Methyl Furan	82
23	31.9	Methyl Vinyl Ketone	70
23	31.9	2,3-Butanedione	86
24	33.0	Acetic Acid	60
24	33.0	Methyl Ethyl Ketone	72
25	34.7	Benzene	78
26	35.2	-----	--
27	36.8	Methyl Isopropenyl-Ketone	84
28	38.5	Phenol	94
29	39.3	Propionic Acid	74
30	40.7	-----	--
31	41.0	3,3-Dimethyl-1-Butene	84
32	41.6	Toluene	92
33	43.2	-----	57



TABLE III: (Con't)

GC Peak	Retention Time	Compounds Identified	Molecular Weight
34	43.9	-----	102
34	43.9	Furfural	96
35	45.7	Furfural	96
36	48.0	-----	--
37	51.5	-----	79
38	53.5	-----	--
39	54.7	Ethyl Benzene	106
40	56.0	1,2(or 1,3 or 1,4)-Dimethyl Benzene	106
41	60.6	Styrene	104
41	60.6	-----	112
42	64.0	-----	---
43	67.8	2-Hydroxy-3-Methyl-2- Cyclopenten-1-One	112
44	76.2	Furyl Methyl Ketone	110
45	79.5	-----	---
46	83.2	-----	---
47	88.0	-----	---
48	99.5	5-Methyl-2-Furaldehyde	110



The data system library search information for the large peak appearing at about 100 minutes retention time is presented in Table IV. These data show the five most probable compounds that fit the mass spectral data for this peak. The best initial fit and refit indicates that the compound created by the presence of the finish is 2-furan carboxaldehyde. It should be noted the refit of the data for two other possible compounds is quite good thereby leaving some question on the absolute identification unverified by a known sample. This compound represents the major change in pyrolysis products and further work could possibly provide an insight into the interaction of the chlorinated polymer with cellulose.

Another of the new peaks resulting from the chlorinated polymer and occurring around 10 minutes retention time was identified as chloromethane as shown in Table V. The presence of this compound has great significance with respect to the purpose of the chlorinated polymer, that is, flame retardance. The identification of a volatile chlorinated compound in the pyrolysis products further confirms the gas phase action of halogen flame retardants compounds.

Due to the numerous equipment and data system breakdowns the other pyrolysis products remain unidentified.

Summary

Cotton duck fabric untreated and treated with four different outdoor finishes were exposed to 200 hours xenon-irradiation. No detectable changes in finish structures were found after 200 hours xenon-arc exposure. The samples were pyrolyzed and the pyrolysis products were separated. The pyrolysis products distribution as shown in Figures 1-11 indicate that the polyethylene finish increases the proportion of propylene and



TABLE IV: MASS SPECTRAL INFORMATION FOR A PYROLYSIS PRODUCT WITH 100 MINUTES RETENTION TIME-FABRIC 106

LIBRARY SEARCH	DATA: VNLS8 #15	BASE M/E 96
SAMPLE: PFK	CALI: VN4 #28	RIC: 5663

25409 Spectra in library NB searched for maximum purity
 288 Matched at least 3 of the 6 largest peaks in the unknown

RANK IN NAME

1	797	2-Furancarboxaldehyde
2	207	1H-Pyrazole,3,5-Dimethyl-
3	19652	1,4-Butanediol,2,3-Bis(Methylene)-
4	2540	2H-Pyran-2-One
5	20503	1H-Imidazole-4-Ethanamine,N,5-Dimethyl-

RANK	FORMULA	M.	WT	B.	PK	PURITY	FIT	RFIT
1	C5. H4. O2		96		96	910	915	991
2	C5. H8. N2		96		96	687	691	987
3	C6. H10. O2		114		96	640	651	840
4	C5. H4. O2		96		96	613	618	929
5	C7. H13. N3		139		96	578	645	783

TABLE V: MASS SPECTRAL INFORMATION FOR A PYROLYSIS PRODUCT WITH 10 MINUTES RETENTION TIME-FABRIC 106

LIBRARY SEARCH	DATA: VNS11 #114	BASE M/E	50
	CALI: CALIWEH #9	RIC:	27487
SAMPLE: PFK			

25409 Spectra in library NB searched for maximum purity 141 matched at least 3 of the 8 largest peaks in the unknown

RANK IN NAME

1	257	Methane, Chloro-
2	3849	1-Buten-3-Yne
3	2251	1,3-Butadiyne
4	1117	Acetaldehyde, Chloro-
5	428	Acetic acid, Chloro-

RANK	FORMULA	M.	WT	B.	PK	PURITY	FIT	RFIT
1	C. H3. CL		50		50	956	959	970
2	C4. H4		52		52	742	767	766
3	C4. H2		50		50	695	735	730
4	C2. H3. O. CL		78		50	604	618	969
5	C2. H3. O2. CL		94		50	471	481	947



methyl isopropenyl-ketone. The chlorinated polymer finish produced new peaks, chloromethane, possibly 2 furan carboxaldehyde and one unidentified, and caused a reduction in methyl isopropenyl-ketone as well as an increase in another peak. The addition of antimony oxide had a minor effect on the pyrolysis products produced when compared to those from the fabric with the chlorinated finish, resulting in an increase in one peak and reduction of another. Both peaks were affected by the chlorinated polymer inversely. The trimethylol finish caused a reduction in peak 22, 2-methylfuran, and increased four others. The xenon-arc exposure had very little influence on the ratio of pyrolysis product. Discussion of the chemical nature of the interaction of the finishes with the cotton cellulose would not be appropriate due to lack of more detailed information and the indication of little overall effect of the finishes of the pyrolysis data.



Bibliography

1. Appleby, Dorothy K., "The Action of Light on Textile Materials: A Review of Literature", American Dyestuff Reporter, 38: 149-156 (1949).
2. Bogaty, Herman. "Deterioration of Cotton Textiles Exposed to Weathering", American Dyestuff Reporter, 38: 253-259 (1949).
3. Byrne, G., Gardiner, D. and Holmes, F. H., "The Pyrolysis of Cellulose and the Action of Flame-Retardants", Journal of Applied Chemistry, 16, 81 (1966).
4. Connor, C. J., R. J. Harper, Jr., A. M. Walker and R. J. Bryson. "Weathering Characteristics of Fabrics Treated with Various Fungicides", Industrial Fabric Products Review, 52, 8: 17, 19-20 (1976).
5. Garn, P. D. and Denson, C. L., "Pyrolysis Products from Cellulose Treated with Flame Retardants. Part I: Halogen-Containing Flame Retardants", Textile Research Journal, 47, 485 (1977).
6. Garn, P. D. and Denson, C. L., "Pyrolysis Products from Cellulose Treated with Flame Retardants. Part II: Nitrogen-Containing Flame Retardants", Textile Research Journal, 47, 535 (1977).
7. Garn, P. D. and Denson, C. L., "Pyrolysis Products from Cellulose Treated with Flame Retardants. Part III: Ancillary Studies", Textile Research Journal, 47, 591 (1977).
8. Howard, J. W. and F. A. McCord. "Cotton Quality Study IV: Resistance to Weathering", Textile Research Journal, 30: 75-117 (1960).
9. Irvine, A. E. "The Use of Chlorinated Paraffins in Rendering Fabric Resistance to Fire-, Water-, and Mildew", American Dyestuff Reporter, 33: 189-192 (1944).
10. Reagan, Barbara M. and Constance M. Chiasson. "Photo-degradation of Flame-, Water-, Weather-, and Mildew-Resistant Cotton Tentage Fabrics", Textile Research Journal, 47: 273-346 (1977).
11. Robinson, Helen M. and Wilson A. Reeves. "A Survey of the Effects of Light on Cotton and Other Cellulose Fabrics", American Dyestuffs Reporter, 51: 17-31 (1961).
12. Slaten, B. L., Spivak, S. M., and Smith, B. F., "The Effects of Weathering and Atmospheric Pollutants on Cotton Fabric and Cotton Fabric Treated with Selected Flame Retardants. I. Physical, Chemical and Flammability Properties", Journal of Applied Polymer Science, 23, 695-716, (1979).





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